Effect of molecular weight on rolled high density polyethylene: 2. Fracture

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In a previous paper, the effect of molecular weight on the structure, morphology and anisotropic behaviour of high density polyethylene (HDPE) has been studied. Entanglements among tie chains connecting the lamella blocks were believed to be the factor that initiated the intrinsic differences. A further study of the fracture behaviour was carried out. It was found that samples with low molecular weight showed brittle fracture with only a small amount of fracture energy being consumed. For high molecular weight samples, a large plastic deformation was associated with the crack extension. The energy consumed for crack extension was almost proportional to the molecular weight. Further stretching of the samples after rolling resulted in a different fracture mechanism and samples showing ductile fracture changed into brittle failure. The morphology of the fracture surface was also studied. It was found that two types of fracture surface existed even for samples with brittle fracture. The fractography was strongly related to the fracture energy. The fracture surface of the ductile failure type samples showed a fibrillar structure. It is suggested that peeling the plastically deformed part off the undeformed surface was the fracture mechanism for the high molecular weight samples. The fracture energy of HDPE without the effect of entanglement was obtained by extrapolating the fracture energy down to zero molecular weight to yield a value of $\sim 370\,\mathrm{J\,m^{-2}}$.

(Keywords: high density polyethylene; molecular weight; fracture; rolled; anisotropy)

INTRODUCTION

It is known that the extension of polymers results in orientation of the polymer chains and anisotropic properties which extend the application of polymeric materials. The structure and mechanical behaviour of oriented polymers have been widely studied. Irrespective of whether the material is drawn or rolled, it possesses higher strength in the machine direction (MD) than in the transverse direction (TD).

At temperatures higher than the glass transition temperature (T_g), the fracture mechanism is most likely due to the separation of the chains after some degree of plastic deformation rather than due to chain breakage. The fracture of isotropic polymers has been studied extensively. Williams[1] applied the ASTM method and derived the critical stress intensity factor (K_{IC}) and the J-integral (J_{IC}) of various polymers over a wide temperature range. Andrews[2] dealt with generalized fracture mechanics which involved the critical energy release rate. This value, the authors believe, should be considered as the critical energy to initiate crack propagation. Cotterell proposed the essential work theory which is basically an evaluation of the crack propagation energy inside the plastically deformed area[3,4]. These methods have been discussed in a previous paper[5]. For oriented polymers, the above methods cannot be applied due to the anisotropic behaviour of the samples. Fracture of the sample along the chain axis (MD) is quite different from fracture perpendicular to the MD (TD). Tearing is one of the methods that has been applied to both isotropic and oriented polymers. It is believed that by extrapolating the tear energy to zero thickness, the fracture energy without any effect from plastic deformation can be derived. Sims[6] has applied tearing to isotropic polypropylene and obtained the tear energy ($\sim 80\,\mathrm{kJ\,m^{-2}}$) at room temperature. The value obtained was close to our value[5]. Decreasing the test temperature has a similar effect to increasing the orientation of the samples in decreasing the tear energy in the MD. Anderton and Treloar[7] tore oriented polyethylene along the MD and found that the tear energy decreased with increase in birefringence. That is to say, the higher the orientation, the less energy is consumed during fracture along the chain axis. They obtained a fracture energy of $712\,\mathrm{J\,m^{-2}}$ for high density polyethylene (HDPE) with a birefringence of >0.03. The fracture energy for low density polyethylene (LDPE) was somewhat lower than that of HDPE. According to Anderton, the value of $712\,\mathrm{J\,m^{-2}}$ was the smallest fracture energy for oriented HDPE obtained in their study. Chiu *et al.*[8] carried out a similar experiment on both quenched and annealed HDPE. Even though it is claimed that tearing the oriented polymer is difficult by tearing in the TD, Gent and Jeong[9] studied the tear strength of some oriented crystalline polymers by tearing along the MD and also along the TD. They found that the tear energy also decreased with increasing draw ratio when tearing the specimens along the MD but the value was larger than that obtained by Anderton. The converse was true for tearing along the TD. These studies showed the effect

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of the extent of orientation on the tear energy. Other properties affecting fracture have received less attention. For tearing, in order to derive the energy without including the energy from plastic deformation, it is necessary to use samples with various thicknesses.

In the first paper of this series[10], the effect of the molecular weight on the structure, morphology and mechanical properties of rolled HDPE was studied. The following facts were obtained.

1. The higher the molecular weight, the higher the orientation of the *c*-axis in the roll direction. The *a*-axis is oriented in the thickness direction (ND). Slippage of the chains along the (1 0 0) plane results in inclination of the lamella normal from the chain axis and the incline angle increases with increase in the molecular weight.
2. The low molecular weight samples show fibrillar structure after peeling off the surface layer while the high molecular weight ones show a smooth fracture surface with evidence of plastic deformation.
3. Even the orientation is more intense for the high molecular weight samples: the anisotropic behaviour of the samples from mechanical testing is not so distinct compared with that of the low molecular weight samples.
4. Further stretching after rolling results in higher orientation and higher anisotropic behaviour. This process could result in a different structure when compared with a sample with the same molecular weight that has undergone rolling only.

It is suggested that the higher the molecular weight, the more entanglements there are among the tie chains connecting the lamella blocks. During rolling, the tie chains transduce more shear stress to the lamella blocks and this results in higher orientation as well as greater chain slippage for high molecular weight samples. The existence of these entanglements also induces easier plastic deformation and lower crystallinity.

In this paper, the effect of molecular weight on the fracture of rolled HDPE is studied for single edge cracked samples. Only fracture along the MD will be discussed to avoid complicated plastic deformation during crack propagation.

EXPERIMENTAL

HDPE with five molecular weight values was supplied by Toso Ltd. The molecular weights were 7.4×10^4, 17×10^4, 42×10^4, 61×10^4 and 98×10^4 (samples 1–5, respectively), and the molecular weight distribution was ~ 2. The samples were pressed at 200°C and then quenched in water. The as-pressed samples were 3 mm thick and were rolled at 115°C (samples 1–3) or 125°C (samples 4 and 5). Due to retraction of the materials, the rolled samples had different thicknesses and thus different birefringences. Samples 2 and 3 were further stretched in the MD direction after rolling to obtain a similar birefringence to that of sample 1. For samples 2 and 3, the rolled samples will be referred to as 2a and 3a and the samples that were further stretched will be referred to as 2b and 3b.

The specimens were cut from the processed samples. The dimensions are shown in *Figure 1*. Initial cracks with different lengths were made by carefully pushing a razor to form sharp cracks from the edge of the specimen. After the test, the ligament length was measured by a microscope. The test speed was 3 mm min^{-1} and the total energy consumed was calculated from the area under the load–displacement curve. The fracture surface was then examined using a scanning electron microscope (Jeol JSM-820).

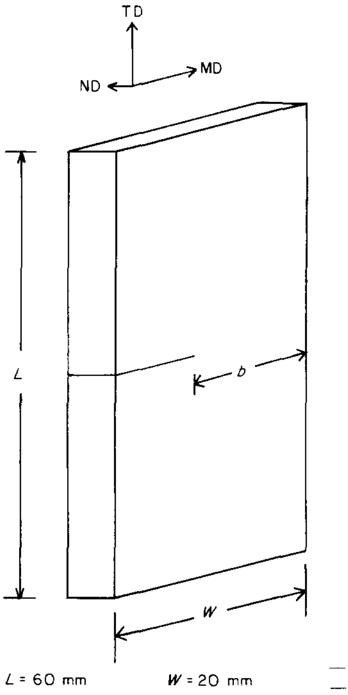

Figure 1 Schematic representation of the dimensions of the sample between the gauges: MD, machine direction; TD, transverse direction; ND, thickness direction

Table 1 Basic properties of the samples

No.	M_w ($\times 10^4$)	ρ (g cm^{-3})	C^a (%)	Δ^b	$\sum n$	$T_{\mathrm{proc.}}$ (°C)
1	7.4	0.968	78.7	0.0499	1.546	115
2b	17	0.964	75.9	0.0510	1.544	115
3b	42	0.963	75.0	0.0496	1.544	115
2a	17	0.962	74.6	0.0472	1.544	115
3a	42	0.954	69.3	0.0418	1.541	115
4	61	0.956	70.6	0.0396	1.542	125
5	98	0.955	69.7	0.0410	1.543	125

[a] Crystallinity
[b] Birefringence ($n_{\mathrm{MD}} - n_{\mathrm{TD}}$)

RESULTS AND DISCUSSION

Fracture energy

The basic properties of the samples are shown in *Table 1*. Rolling results in an increase in density. The sum of the refractive indexes from the MD, TD and thickness direction (ND) was almost a constant. Two types of fracture were observed. The fractured pieces and the load–displacement curves are schematicaly shown in *Figure 2*. Type I fracture was the brittle type and the specimen fractured suddenly. Type II fracture was the ductile type so that a large extent of plastic deformation occurred first, followed by the separation of the upper and lower pieces. The latter showed a sudden drop in load. Samples 1, 2a, 2b and 3b belonged to type I fracture while samples 3a, 4 and 5 belonged to type II fracture. The fracture energy of types I and II was analysed in different ways. For type I, the energy consumed by plastic deformation was assumed to be small and therefore not

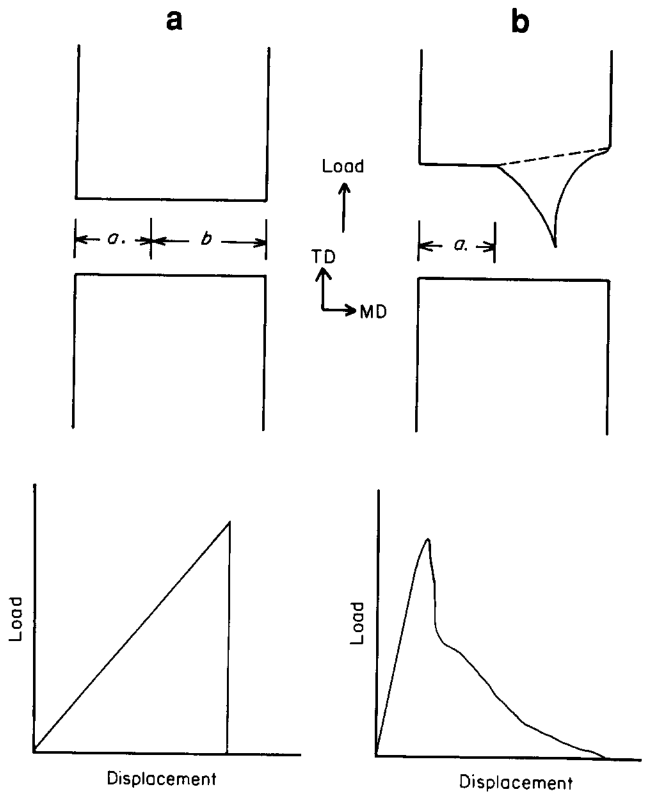

Figure 2 Schematic representation of (a) brittle and (b) ductile fracture. The upper diagrams show the fractured specimens while the lower diagrams are the load–displacement graphs

considered. For type II, the large plastic deformation could not be neglected and was subtracted from the total energy.

Type I. The fracture energy per ligament area, γ, was used as the unit. It was obtained by dividing the work input to the system by the ligament area. With specimens of various initial crack length, a plot of energy/thickness (U/t) *versus* ligament length (b) could be obtained and the slope was γ. *Figure 3* shows the results for type I samples. It should be noted that the smaller the molecular weight, the smaller the value of γ. Further stretching of sample 2 resulted in less fracture energy, which decreased from 1.05 to 0.55 kJ m^{-2}.

Type II. A typical fracture process of this type is shown in *Figure 4*. *Figure 4a* is at the beginning of testing. When the load reached the maximum, as shown in *Figure 2b*, a slip band initiated from the crack tip and crossed the sample, as shown in *Figure 4b*. The next step was the enlargement of the slip band while separation of the plastically deformed and undeformed parts occurred (*Figure 4c*). One edge of the slip band was always at the tip of the crack. Finally, the process ended with the fracture surface of the undeformed part parallel to the roll direction (*Figure 4d*). It is suggested that, instead of type I fracture, the sample failed in the peeling of plastically deformed chains off the undeformed surface. If this is the mechanism, the molecular chains of the

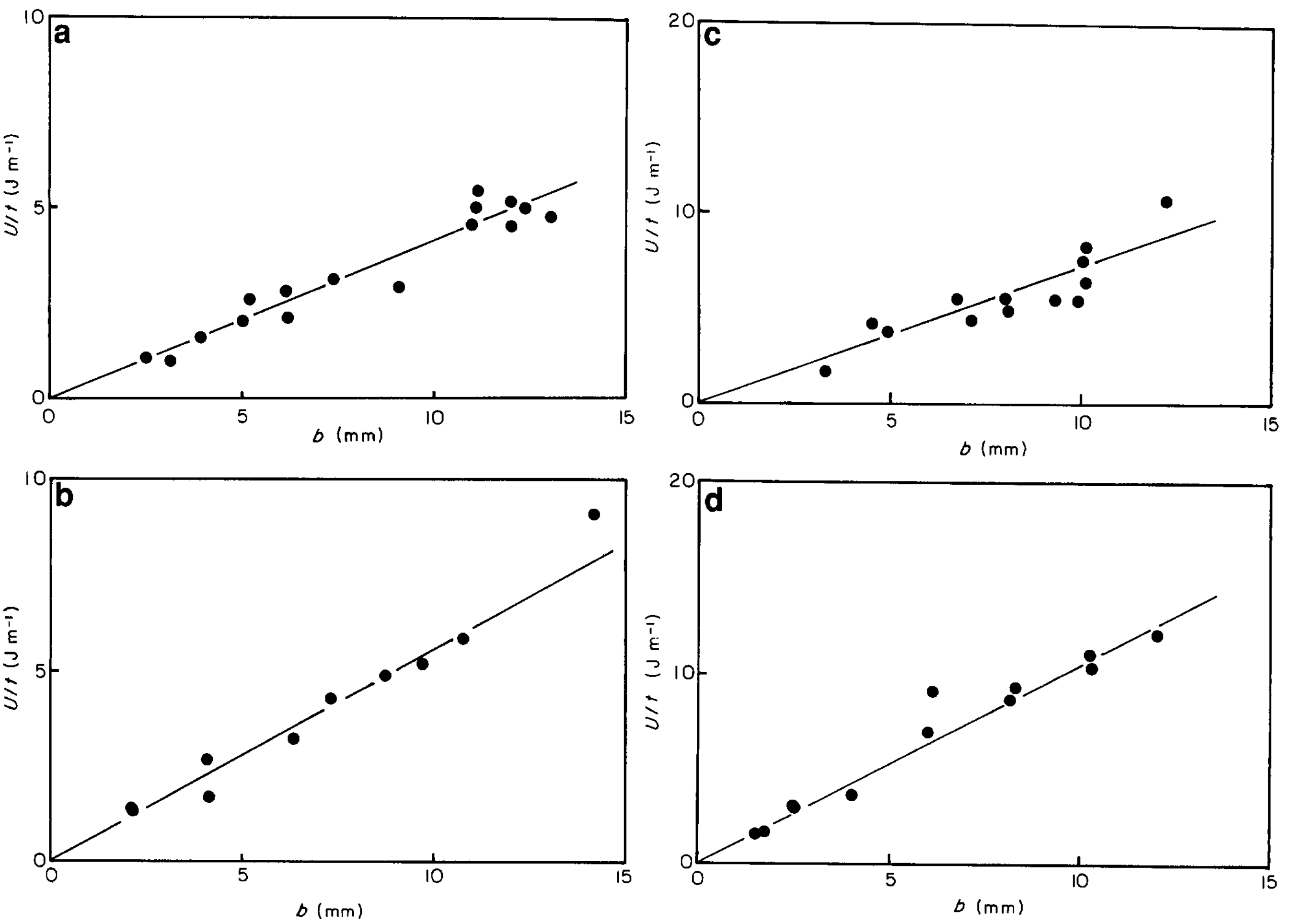

Figure 3 Plots of U/t *versus* b of the brittle fracture type for samples: (a) 1 ($\gamma = 0.41$ kJ m^{-2}); (b) 2a ($\gamma = 0.55$ kJ m^{-2}); (c) 2b ($\gamma = 0.71$ kJ m^{-2}); (d) 3b ($\gamma = 1.05$ kJ m^{-2})

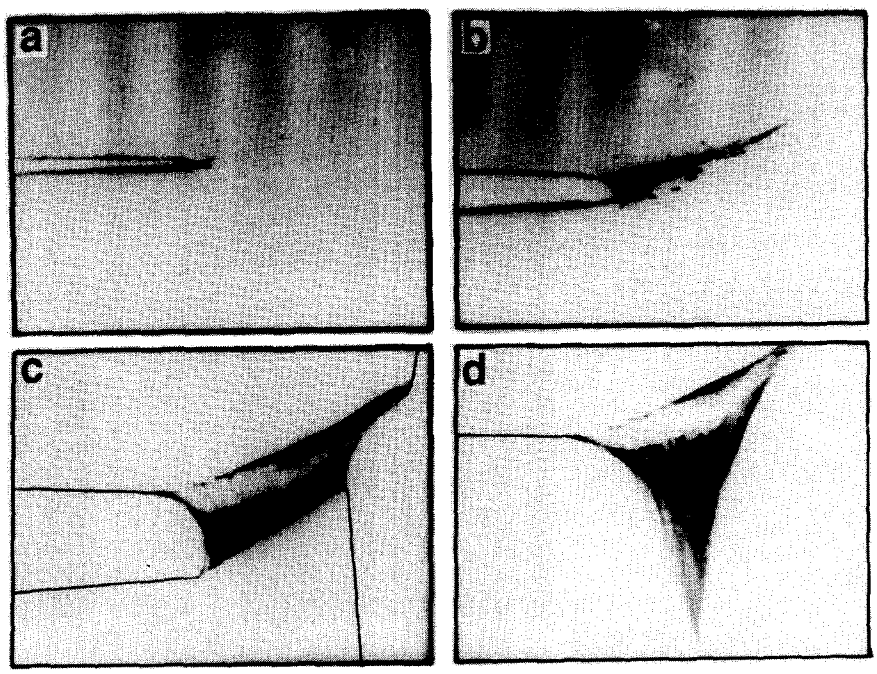

Figure 4 Fracture process of the ductile fracture type: (a) at the beginning of the test; (b) a deformed band initiated from the crack tip and extended through the ligament with some inclined angle off the crack plane; (c) after the deformed band went through the ligament, it began to expand while peeling of the plastically deformed part off the undeformed part occurred; (d) completion of the fracture

plastically deformed part should be reoriented from the roll direction towards the test direction. This was confirmed by wide angle X-ray diffraction (WAXD) patterns from the plastically deformed part. *Figure 5* shows the WAXD patterns by shooting the X-rays from the ND and the positions where the WAXD pictures were taken from. Positions 1, 2 and 3 were inside the plastically deformed area while position 4 was on the outside of it. The roll direction was in the horizontal direction. Comparison of the WAXD patterns from positions 1, 2 and 3 with that from position 4 clearly shows reorientation of the chain axis as suggested above. It is impossible to argue whether the separation of chains occurred before plastic deformation. If that were the case, plastic deformation would not have been so extensive since the materials would have failed in brittle fracture with a smaller amount of energy consumed. It is assumed that the plastic deformation shown in *Figure 4* consumed the same energy per unit volume for any element of the sample. Thus the total energy (U_t) obtained is composed of two parts: one is the energy from plastic deformation (U_{plastic}); the other is the energy consumed during chain separation (U'_c). Hence, U_t can be expressed as:

$$U_t = U_{\text{plastic}} + U'_c \qquad (1)$$

Furthermore, U_{plastic} can be expressed in terms of the energy of plastic deformation per unit volume, U_p:

$$\begin{aligned} U_{\text{plastic}} &= U_p \Delta V \\ &= U_p(\Delta A \times t) \qquad (2) \end{aligned}$$

where t is the original thickness of the rolled sample and ΔA is the area where the plastic deformation originated from. U'_c can also be rewritten as:

$$U'_c = U_c(b \times t) \qquad (3)$$

where b is the length of the ligament and U_c is the fracture energy per unit ligament area. Substituting equations (2) and (3) into equation (1) and dividing the two sides by the area of the ligament ($b \times t$), one obtains:

$$U_t/bt = U_c + U_p(A/b) \qquad (4)$$

Therefore, from a plot of U_t/bt *versus* A/b, one is able to derive the value of U_c ($= U'_c/bt$). *Figure 6* shows such plots for samples 3a, 4 and 5. It was found that the smaller the molecular weight, the smaller the U_c for these samples with similar birefringence values.

For both types I and II, the fracture energies are represented as the energy per unit ligament area. In this way, the fracture energies of these two types can be compared. *Figure 7* shows a plot of the fracture energy *versus* molecular weight. The samples fell into two groups, as shown by the straight lines. The first group was that of samples with similar birefringence which failed with type I fracture except for sample 2a. The least square linear regression result can be expressed as:

$$\gamma = 8.214 \times 10^{-7} M_w + 0.375 \qquad (\text{kJ m}^{-2}) \qquad (5)$$

The second group was that of type II samples and the linear regression result is:

$$\gamma = 3.797 \times 10^{-6} M_w + 0.368 \qquad (\text{kJ m}^{-2}) \qquad (6)$$

As discussed previously, the higher the molecular weight, the greater the number of entanglements. The structure, morphology and mechanical properties were affected by the existence of more entanglements for high molecular weight samples. The intercepts from equations (5) and (6) possess the physical meaning of the fracture energy without any effect from entanglements since the intercepts were extrapolated to zero molecular weight. It is encouraging to see that the intercepts are similar. Deviation of sample 2a from type I samples will be discussed after the fracture surface is examined. It is suggested that this fracture energy along the chain axis should be the energy for chain separation per unit area of

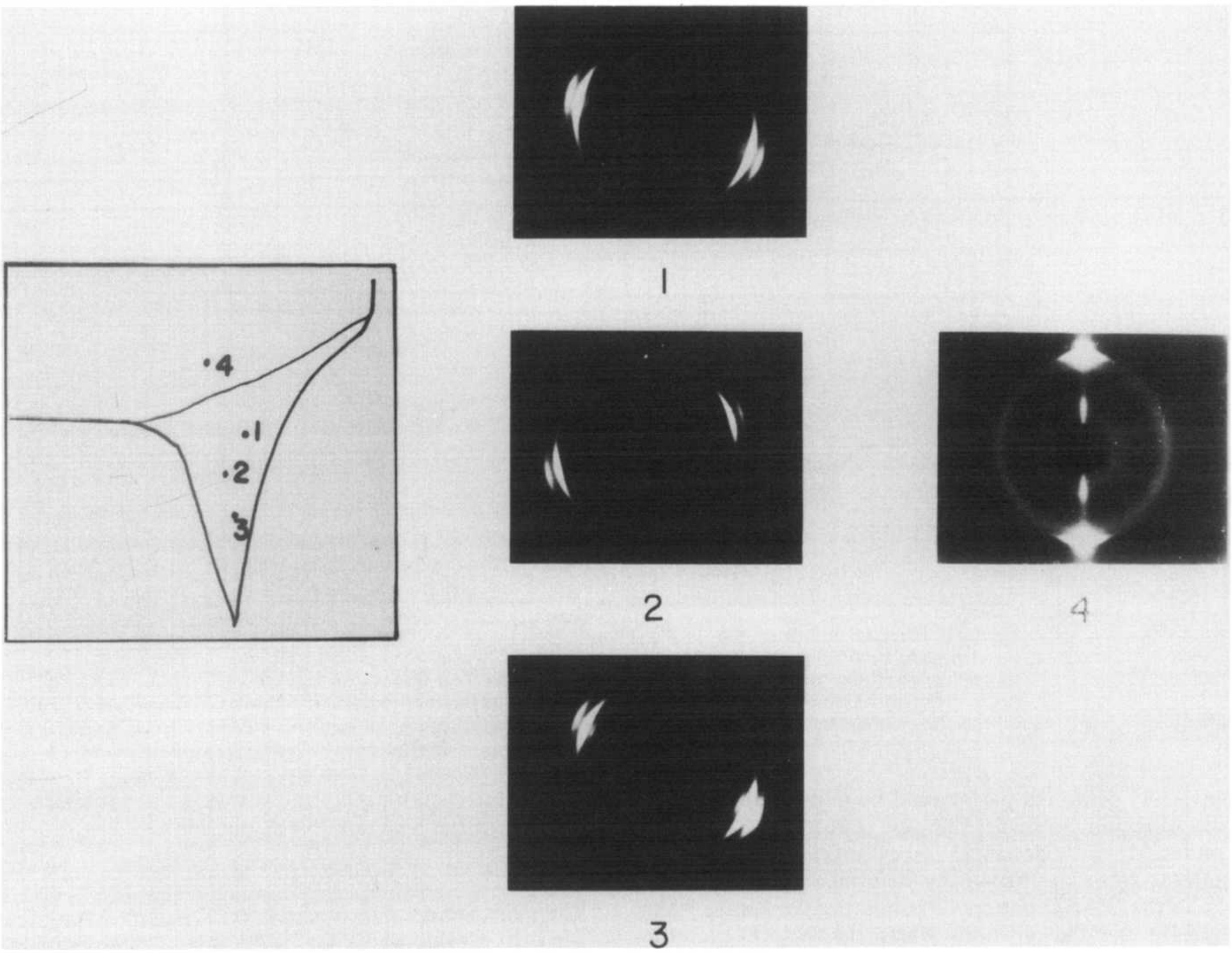

Figure 5 WAXD patterns showing the orientation of the plastically deformed parts: (a) schematic representation showing positions where the WAXD patterns were taken from; (b) WAXD patterns corresponding to positions in (a); (c) WAXD patterns of the undeformed part

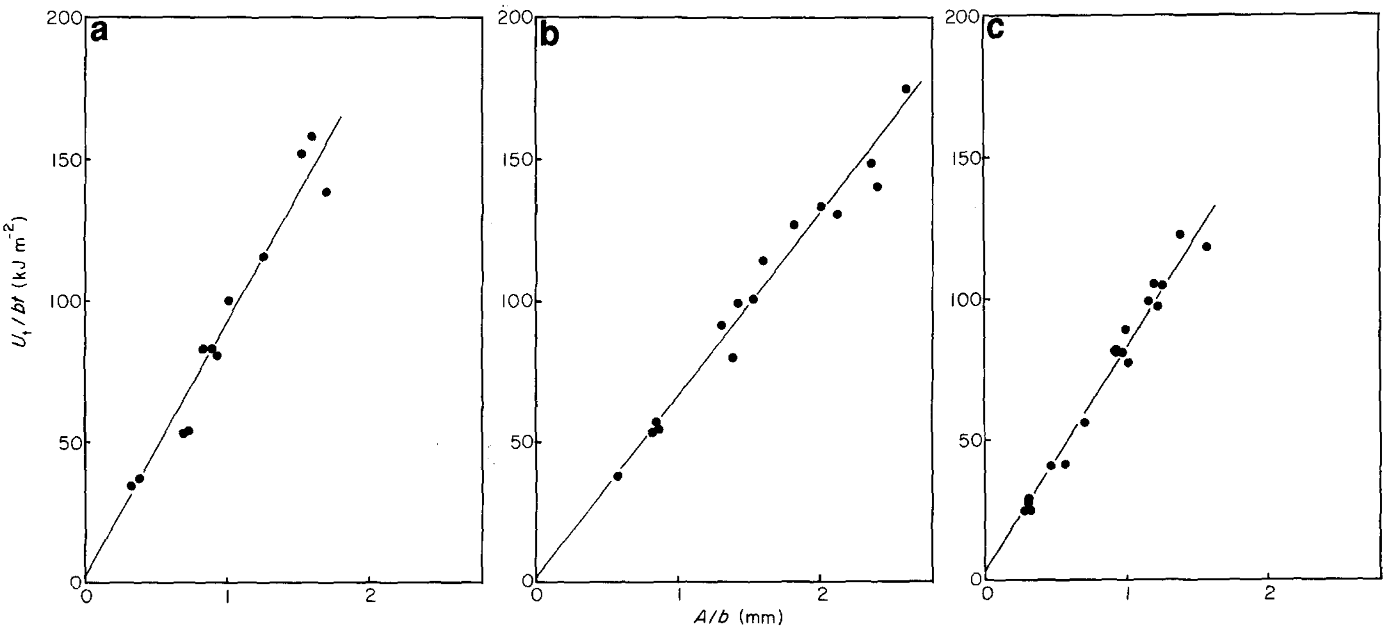

Figure 6 Plots of U_t/bt *versus* of the ductile fracture type for samples: (a) 3a ($U'_c/bt = 1.9$ kJ m^{-2}); (b) 4 ($U'_c/bt = 2.7$ kJ m^{-2}); (c) 5 ($U'_c/bt = 4.1$ kJ m^{-2})

HDPE without any effect from plastic deformation or entanglements.

Even though the fracture proceeded along the chain axis, the slip band that initiated the global plastic deformation, as shown in *Figure 4b*, inclined from the roll direction. For isotropic materials, the stress at the crack tip can be derived from linear fracture mechanics. For an anisotropic continuum, it is much more complicated. Although the chains were highly oriented in this study, entanglements existed among tie chains that connected the lamella blocks and transduced energy was input into the system not only in the MD but also in the TD. This complicated the stress distribution at the crack tip. At present it is difficult to conclude if the shear stress or the shear strain shows a maximum in the direction of the slip band. The mechanics of the process is now being studied.

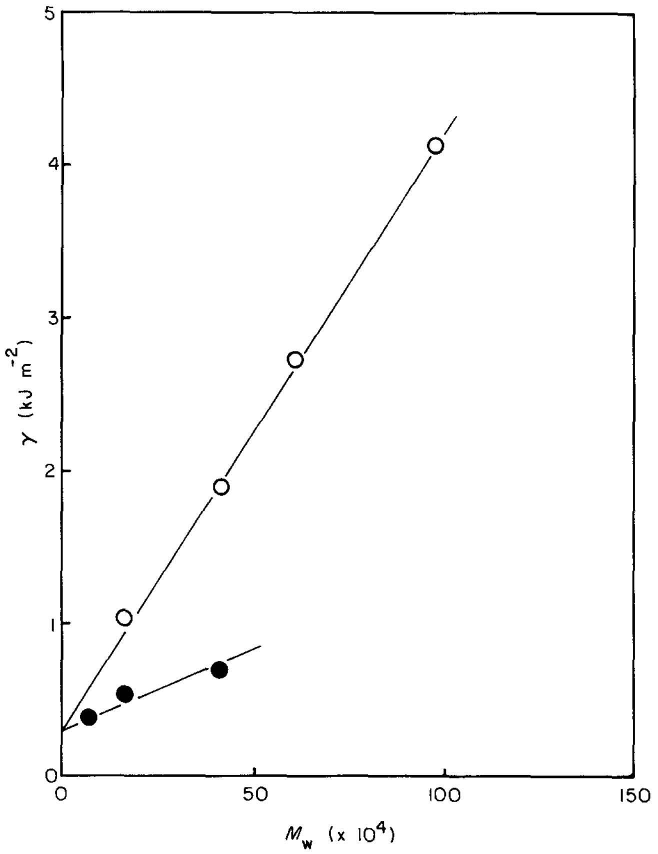

Figure 7 Plot of the fracture energy *versus* molecular weight. Samples of (○) ductile and (●) brittle fracture

Morphology

The morphology of the fracture surface was quite informative. The morphology can be categorized into brittle type corresponding to type I fracture and ductile type corresponding to type II fracture.

Brittle type. This type includes samples 1, 2a, 2b and 3b. The fracture surface of this type could be further divided into two patterns. The first pattern is shown in *Figure 8a*. Strips with plastically deformed parts can be observed. This pattern was found to exist close to the initial crack tip. The second pattern is shown in *Figure 8b* which exhibits few plastic deformation residues. This pattern existed further away from the initial crack tip. The intersect of these two patterns could be clearly distinguished and is shown in *Figure 8c*. For samples 1, 2b and 3b, the first pattern occupied only a small part of the ligament and the second pattern occurred in the rest ligament. The first pattern covered most of the ligament area for sample 2a and this is believed to be the reason why the fracture energy of sample 2a was higher than that of the other samples showing type I fracture. It is suggested that before the sudden fracture, some crack opening occurred. Because the material was highly oriented and with weaker connections between the lamella blocks, crazing along the fracture plane occurred more easily than the large amount of plastic deformation around the crack tip. Coalescence of the fibrillar crazes resulted in a large crack and induced catastrophic fracture. The first pattern was considered to be the residues of such crazes. Sample 1 possessed the lowest molecular weight and highest crystallinity. From our previous paper[10], this material was suggested to possess less entanglements among the tie chains connecting the lamella blocks. Separation of the molecular chains was easier than creating plastic deformation. Thus the first pattern fracture surface occupied only a very small part of the ligament of sample 1. For sample 2a, the molecular weight was higher and more entanglements existed leading to a larger fracture energy which was partly consumed due to more plastic deformation. For sample 3a, the molecular weight was even higher and the fracture mechanism did not fall into this type.

Ductile type. This type includes samples 3a, 4 and 5. Only one fracture pattern, as shown in *Figure 9a*, was observed for all these samples. This pattern existed throughout the ligament. Separation of bundles of fibre seemed to be the fracture mechanism. The fracture surface

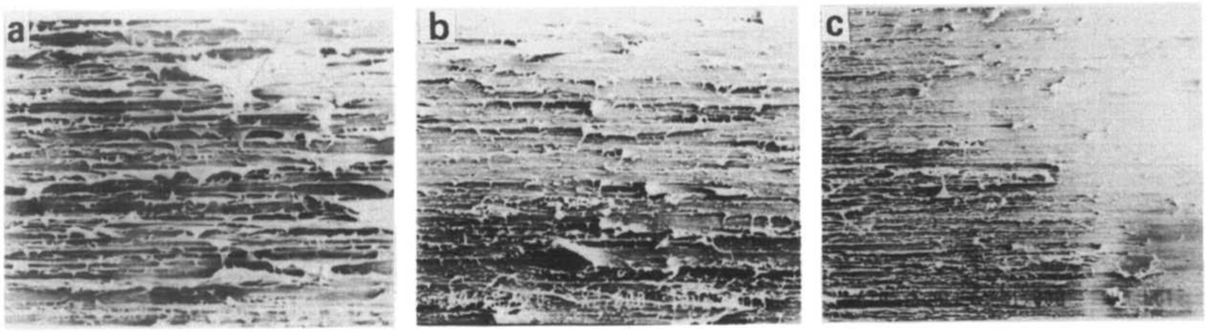

Figure 8 Fracture surface of the brittle fracture type: (a) pattern I; (b) pattern II; (c) boundary between patterns I and II. Magnification: (a, b) 2000 ×; (c) 1000 ×

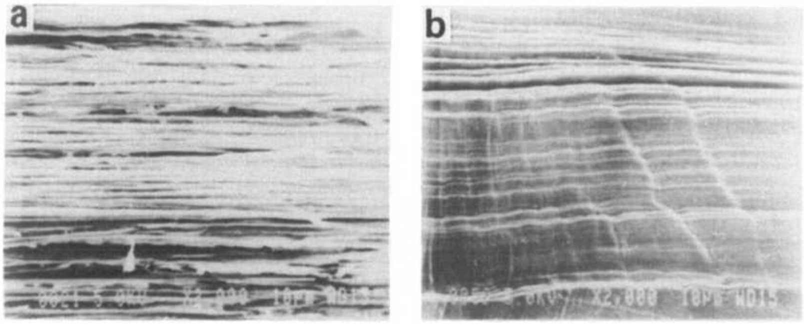

Figure 9 Fracture surface of the ductile fracture type (a) and of the plastically deformed part (b). Magnification 2000×

of the undeformed part was exactly the same as that of the plastically deformed part. *Figure 9b* shows the plastically deformed surface region close to the crack plane. For this type of fracture, the samples possessed high molecular weight. The entanglements along the molecular chains prevented the brittle failure as discussed above. Plastic deformation occurred in the form of a slip band first and then expanded with the separation of the fracture surfaces.

CONCLUSIONS

The fracture of rolled HDPE with various molecular weights was studied. It was found that the smaller the molecular weight, the smaller the fracture energy. After subtracting the energy consumed due to global plastic deformation, the energy per ligament area consumed was found to be proportional to the molecular weight. From studying the morphology, it is suggested that the existence of entanglements among tie chains connecting the lamella blocks for high molecular weight samples resulted in plastic deformation and prevented brittle fracture. The fracture energy along the chain axis of HDPE without effect from entanglements can be derived by extrapolating the fracture energy to zero molecular weight. This fracture energy is $\sim 370\,\mathrm{J\,m^{-2}}$ at room temperature.

REFERENCES

1 Williams, J. G. 'Fracture Mechanics of Polymers', Ellis Horwood Ltd, Chichester, 1984
2 Andrews, E. H. *J. Mater. Sci.* 1974, **9**, 887
3 Cotterell, B. and Reddel, J. K. *Int. J. Fracture* 1977, **13**, 267
4 Mai, Y.-W. and Cotterell, B. *Int. J. Fracture* 1986, **32**, 105
5 Wang, M.-D., Nakanishi, E., Hashizume, Y. and Hibi, S. *Polymer* 1992, **33**, 3408
6 Sims, G. L. A. *J. Mater. Sci.* 1975, **10**, 647
7 Anderton, G. E. and Treloar, L. R. G. *J. Mater. Sci.* 1971, **6**, 562
8 Chiu, D.-S., Gent, A. N. and White, J. R. *J. Mater. Sci.* 1984, **19**, 2622
9 Gent, A. N. and Jeong, J. *J. Mater. Sci.* 1986, **21**, 355
10 Wang, M.-D., Nakanishi, E. and Hibi, S. *Polymer* 1993, **34**, 2783